

NOTE

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Chemical characteristics of surfaces of hardwood and softwood deteriorated by weathering

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Abstract The factors that cause weather-induced deterioration of wood surfaces were determined by chemical and spectroscopic analyses. Albizzia (*Paraserianthes falcata* Becker.) and sugi (*Cryptomeria japonica* D. Don) were exposed to two temperate conditions of natural weathering with and without rainfall and to accelerated conditions of artificial weathering coupled with ultraviolet (UV) light irradiation and water flashing. Infrared spectroscopic analysis showed that the oxidative reaction of lignin was observed under all conditions of weathering for both wood species. However, a marked decrease in lignin and hemicellulose content were recognized when albizzia woods were exposed to weathering with water. Lignin content in the softwood sugi did not decrease as much as in albizzia even in the presence of water, but the modification of lignin macromolecules was assumed to be accelerated by water, as seen by electron spin resonance spectroscopy. These results showed that the presence of water promotes the weathering deterioration of wood under UV irradiation.

Key words Chemical analysis · *Cryptomeria japonica* · ESR analysis · IR spectroscopy · *Paraserianthes falcata* · Weathering

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Introduction

Woody material has been utilized for various purposes, such as engineering and structural works as well as interior and exterior construction materials. However, once exposed to weather, wood undergoes deterioration of its physical properties, with changes in or loss of its characteristic appearance (e.g., color, texture). Such deterioration involves chemical modification of some of the cell wall polymers in wood, such as cellulose, hemicellulose, and lignin. The need to maintain the surface characteristics of wood, which is alternatively exposed to sunshine and rainfall, is increasing because outdoor uses of wood-based materials are expanding.

Weathering is one of the most important factors involved in wood deterioration. When wood is exposed to the outdoors, its components are modified degradatively by a combination of factors, such as light energy, rain, and air oxidation.^{1,2} Many factors are responsible for natural weathering: solar irradiation (ultraviolet, visible, and infrared light), moisture (rain, dew, snow, humidity), temperature, and atmospheric gases including oxygen and pollutant gases (e.g., sulfur dioxide and nitrogen dioxide).³ Among them, ultraviolet (UV) light, the component of sunlight, is suggested to have the most damaging effect by depolymerizing lignin in the wood cell walls,¹ followed by water, which washes away the degradation products, causing surface erosion.

For outdoor applications of wood materials, it is necessary to develop effective methods to avoid weather-induced deterioration by identifying the responsible factors and their effects on weathering deterioration. In this study we examined the chemical characteristics of wood exposed to weathering deterioration under various exposure conditions and wood species. Two wood species with almost the same specific gravity were selected as the test specimens: albizzia (*Paraserianthes falcata* Becker.) and sugi (*Cryptomeria japonica* D. Don). Albizzia is a fast-growing hardwood species planted in the tropics, and sugi is a major softwood species cultivated in Japan.

Materials and methods

Wood samples

Sapwoods of 20-year-old *albizzia* and 25-years-old *sugi* were used at a size of 3 mm (R) \times 45 mm (T) \times 145 mm (L). The surface of the specimens were flattened and smoothed by a planer machine and exposed to weathering immediately after surfaces preparation. The moisture content of the specimens before weathering was about 10%.

Weathering conditions

Natural weathering

Test pieces of *albizzia* and *sugi* were exposed to sunlight with and without rainfall facing to the south and inclined at 45° from the horizon for 1 year (November 1994 to October 1995) on a campus of the Wood Research Institute, Kyoto University, Uji-City, Kyoto, Japan (135° 48'E, 34° 54'N). The average temperature, total rainfall, and amount of sunshine during the exposure period in Kyoto in 1995 were 15.9°C, 1358 mm, and 1713 h, respectively (Amedas Information, 1995).

For natural weathering with rainfall, the samples were placed outside a building without any covering; for temperate weathering without rainfall, the samples were exposed to sunshine under outdoor conditions during sunny days but shaded by a glass cover when it rained to prevent the effect of water.

Artificial weathering

Accelerated weathering was carried out artificially using a commercial chamber machine, the Sun-Shine Super Long-life Weather Meter WEL-SUN-HC (Suga Test Machine Co., Tokyo, Japan), which can be controlled for both light irradiation and water. Specimens were exposed to a 3-kWh carbon arc light through a glass filter that cuts off light below 255 nm. The chamber was kept at 50°C and 50% relative humidity for 1080 h. Distilled water was flashed for 12 min each hour. The temperature of the black-panel was kept at 63°C.

Chemical analysis

Sample preparation

Wood meal samples from the exposed specimens were collected by gently shaving the fragile surface layers using a handknife. The samples were assumed to be prepared from the exposed surface portions with 0.5 mm thickness. The control samples were also prepared from the unexposed woods. The samples were ground with a Wiley mill into powder fine enough to pass through an 80-mesh (177 µm) sieve.

Prior to chemical analysis, the wood meal samples were extracted with ethanol/benzene (1:2, v/v) for 6 h by a Soxhlet extractor.

Lignin content

The lignin content was measured using the acetyl bromide procedure described by Iiyama and Wallis.⁴

Neutral sugar composition analysis

The samples were hydrolyzed with 72% sulfuric acid followed by dilution to 4% according to the method described by Saeman et al.⁵ After hydrolysis, inositol was added as an internal standard for gas chromatographic analysis. Reaction solutions were neutralized with BaSO₄ and filtrated. The filtrate were applied to the ion-exchange resins [Dowex 50 \times 2 (H⁺ form) and Dowex 1 \times 8 (AcO⁻ form)] and then evaporated. Neutral sugars were converted to corresponding alditol acetates⁶ and analyzed by gas-liquid chromatography (GC-12A; Shimadzu, Kyoto, Japan) equipped with a flame ionization detector on a column of 3% OV-225 on Chromosorb W AW-DMCS (80–100 mesh; 2.6 mm \times 2.1 m) (GL Science Co., Tokyo, Japan). Temperature conditions were as follows: injection temperature 230°C, column temperature 200°C, detection block 230°C.

Alkaline nitrobenzene oxidation

Samples were degraded oxidatively with 0.25 ml nitrobenzene and 4 ml 2N NaOH solution at 160°C for 2 h. After cooling, a 3-ethoxy-4-hydroxybenzaldehyde solution was added as an internal standard for gas chromatographic analysis. The reaction mixture was extracted three times with 30 ml CH₂Cl₂ to remove excess nitrobenzene and by-products. The aqueous layer was acidified with 4M HCl solution and then extracted three times with 30 ml CH₂Cl₂. Recovered products were trimethylsilylated with *N*, *O*-bis(trimethylsilyl) acetamide (BSA) and analyzed by gas-liquid chromatography on a column of 2% OV-17 on Chromosorb W AW-DMCS (80–100 mesh; 2.6 mm \times 2.1 m) (GL Science Co.). Temperature conditions were as follows: injection temperature 200°C; column temperature programmed from 140°C to 190°C with 1°C/min, then kept for 5 min at 190°C; detection block 200°C. The contents of the main products were calculated as the percent weight of lignin.

Infrared and electron spin resonance spectroscopic analyses

Wood meals collected from the wood surfaces were dried at 60°C for 12 h over P₂O₅ in a vacuum oven. Infrared (IR) spectra were obtained on an FTIR-7000 spectrophotometer (JASCO Japan, Tokyo, Japan) using the KBr tablet technique.

Electron spin resonance (ESR) spectrometry was conducted using an X-band ESR spectrometer (JES-TE 300, 100 kHz modulation; JEOL, Tokyo, Japan). To avoid the distortion of spectra due to power saturation, measurements were carried out at a microwave power of 0.2 mW. All spectra were recorded under an ambient atmosphere at 77 K using liquid nitrogen.

Results and discussion

Changes in chemical composition

According to the histological observations of Yata and Tamura,⁷ the photodegraded zone with grayish color reached 0.2 mm depth from the surface after weathering for half a year, and a brown zone 0.5 mm thick was found underneath the gray zone. As these two zones were considered to have been directly or indirectly modified by weathering, the samples collected for chemical analysis (within 0.5 mm of the surface of testing specimens) in this study were assumed to be included in the eroded zone of the wood surfaces by weathering.

The results of chemical analysis showed the differences in lignin content between albizzia and sugi wood for the various exposure conditions (Table 1). The lignin content in the albizzia wood surface decreased significantly after exposure to various weathering conditions, especially in the presence of water irrespective of natural or artificial conditions. Xylose, which was a main component of hardwood hemicellulose xylan, showed the same reduction tendency after weathering. It has been reported that the major effect of weathering on wood surfaces was delignification,² and lignin and hemicelluloses were easily decomposed by UV irradiation.⁸ Cellulose was assumed to be protected from photodegradation because coexisting lignin preferentially absorbed UV light and prevented cellulose from being activated by UV.⁹ However, the chemical composition of wood after natural weathering without rainfall demonstrated that the action of water was not negligible, as seen by the de-

creased lignin and hemicellulose contents. It was assumed that UV irradiation of wood surfaces decomposed lignin and formed low-molecular-weight lignin fragments, which would be water-soluble, as reported by Hon and Chang.¹⁰ Water flashing would leach away the lignin fragments together with hemicelluloses as water-soluble lignocellulosic materials. Therefore, as reported by Feist et al.,⁸ the wood surfaces became rich in cellulose, which was confirmed by the increased relative content of glucose after natural and artificial weathering (Table 1).

On the other hand, the lignin content of sugi wood did not decrease as markedly as was observed in albizzia wood. Lignin and mannose contents were significantly changed by weathering conditions. The decreased mannose content revealed a reduction of hemicellulose content in the exposed wood because glucomannan is a major component of hemicellulose in softwood. The relatively increased glucose content suggested that cellulose was kept on the wood surfaces even after being exposed to weathering, as in albizzia wood.

The chemical analysis for both wood species showed an acceleration effect by water flashing on the reduction of lignin and hemicellulose contents. It was noteworthy that there was a marked difference in the resistance against water during weathering between albizzia and sugi; sugi wood was more resistant to lignin and hemicellulose reductions. Aromatic units of lignin in softwoods and hardwoods are composed of guaiacyl and guaiacyl-syringyl, respectively. The susceptibility to weathering deterioration might be different for the two lignin types, with sugi lignin not easily removed during weathering because of side reactions such as condensation.

The changes in hemicellulose contents suggested that hemicelluloses would be removed along with lignin. Lignin and hemicellulose are present in wood cell walls as a lignin-hemicellulose matrix,¹¹ so lignin decomposition would accelerate the loss of hemicelluloses in the matrix during exposure to water.

Alkaline nitrobenzene oxidation

The yields of oxidative products (vanillin, vanillic acid, syringaldehyde, and syringic acid) are shown in Table 2. Total yields of these products did not change as much in the hardwood albizzia as in sugi wood. However, the yield of acidic products increased, as did the syringaldehyde/vanillin (S/V) ratio. In sugi wood the total yield decreased after exposure to weathering, and the acidic product vanillic acid increased. The yields of these nitrobenzene oxidation products suggested a structural change in the residual lignin polymer, such as an increment of condensed structures or the aromatic ring opening. Considered along with the results of sugi woods, the guaiacyl structure was assumed to be easily modified during weathering, which can be supported by the change in the S/V ratio in albizzia woods. In both wood species, yields of acidic products increased probably because of oxidative cleavage between C α and C β of the lignin side chain during exposure to all conditions of weathering.

Table 1. Chemical composition of surface fraction of weathered wood

Condition	Lignin (%)	Glucose (%)	Xylose (%)	Mannose (%)
Albizzia				
Unexposed	26.5	56.8	14.0	1.4
Natural	15.1	74.3	8.6	1.6
Natural without rainfall	22.4	61.9	12.3	2.7
Artificial	8.7	83.0	6.8	1.3
Sugi				
Unexposed	29.1	51.5	1.8	11.2
Natural	20.5	64.6	0.7	8.1
Natural without rainfall	22.2	60.6	2.0	8.7
Artificial	21.5	63.1	1.2	8.1

"Natural," "natural without rainfall," and "artificial" indicate natural weathering with rainfall, natural weathering without rainfall, and artificial weathering, respectively.

Table 2. Yields of nitrobenzene oxidation products of the surface fraction of weathered wood

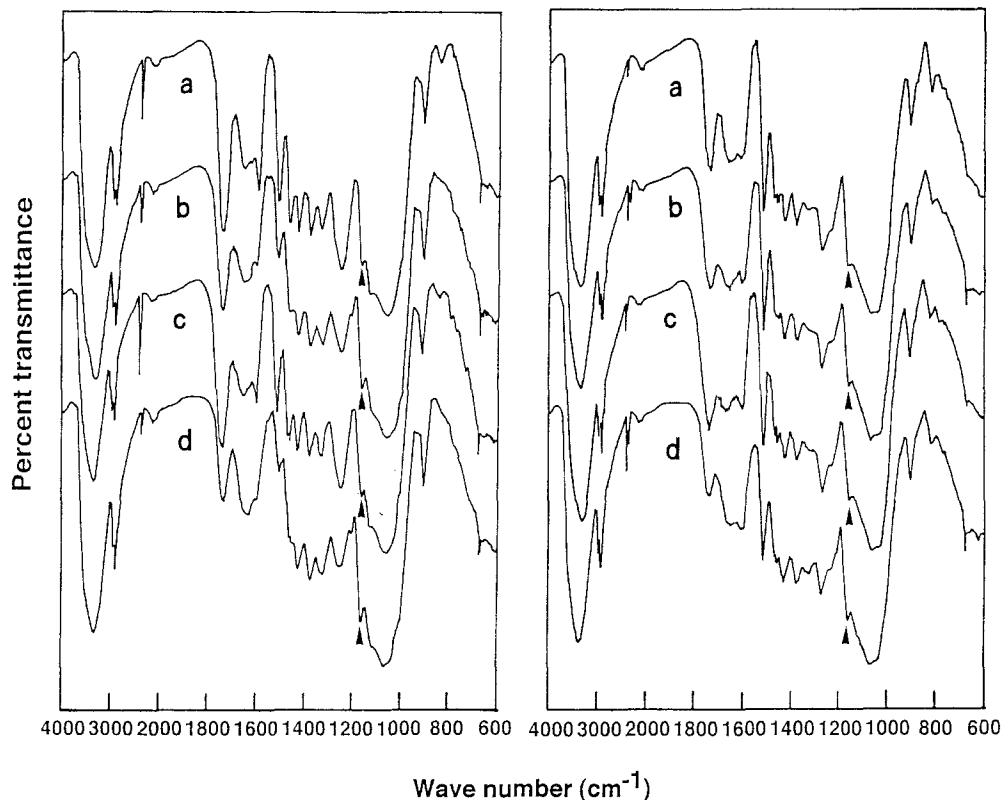
Condition ^a	Vanillin (%)	Vanillic acid (%)	Syringaldehyde (%)	Syringic acid (%)	Total (%)	S/V ratio
<i>Albizia</i>						
Unexposed	6.7	0.7	17.1	1.2	25.7	2.49
Natural	3.9	1.5	16.0	3.4	24.8	3.80
Natural without rainfall	4.3	1.5	18.6	3.5	27.9	3.77
Artificial	5.3	1.7	13.9	5.4	26.3	2.78
<i>Sugi</i>						
Unexposed	20.8	1.5	—	—	22.3	—
Natural	13.6	4.1	—	—	17.7	—
Natural without rainfall	17.3	2.3	—	—	19.6	—
Artificial	16.4	3.5	—	—	19.9	—

Values were calculated as percent per lignin

^aSee footnote to Table 1

S/V, syringaldehyde/vanillin

Fig. 1. Infrared spectra of albizia (left) and sugi (right) woods before and after weathering. The peaks of 1160 cm^{-1} are indicated by arrowheads. *a*, unexposed; *b*, natural weathering with rainfall; *c*, natural weathering without rainfall; *d*, artificial weathering



Spectroscopic analysis

The infrared spectra of wood surface samples before and after weathering are shown in Fig. 1. The relative intensities of major bands with respect to a peak at 1160 cm^{-1} due to a glucopyranose ring vibration are shown in Table 3 for semiquantitative evaluation of absorption changes, according to Hon and Feist.¹²

The intensity of the peak at around 1510 cm^{-1} , which originated from the aromatic ring structure of lignin,¹³⁻¹⁶

decreased during each weathering process for both wood species, indicating decomposition or removal of lignin as shown by chemical analysis. The intensity of the peak at 1600 cm^{-1} , which was also due to C=C aromatic ring vibration, did not decrease as markedly as that of 1510 cm^{-1} . As this peak intensity was affected by conjugated carbonyl structures,¹⁵ carbonyl generation was assumed to occur. However, the peak at 1650 cm^{-1} due to carbonyl stretching in lignin did not become as large after weathering (Fig. 1, Table 3). To examine the carbonyl generation in lignin, the

Table 3. Relative peak intensities of infrared absorbances of surface fraction of weathered wood

Condition ^a	A/A1160cm ⁻¹					
	1739	1650	1600	1510	1240	830
Albizia						
Unexposed	1.81	1.15 (1.18)	1.33 (1.37)	0.97	0.82	0.17
Natural	1.20	0.95 (2.72)	0.77 (2.22)	0.35	0.40	0.05
Natural without rainfall	1.59	1.06 (1.33)	1.13 (1.42)	0.80	0.72	0.11
Artificial	0.84	0.91 (4.39)	0.75 (3.60)	0.21	0.33	0.03
Sugi						
Unexposed	1.26	1.16 (1.12)	1.12 (1.08)	1.03	0.53	0.32 ^b
Natural	1.18	1.11 (1.15)	1.05 (1.09)	0.96	0.47	0.15 ^b
Natural without rainfall	1.53	1.32 (1.28)	1.26 (1.22)	1.03	0.56	0.20 ^b
Artificial	0.76	0.91 (1.17)	0.89 (1.14)	0.78	0.39	0.16 ^b

Values in parentheses were obtained from A/A1510cm⁻¹^aSee footnote of Table 1^bAt 810, not 830

relative intensities of these peaks with respect to that of 1510cm⁻¹ are shown in parentheses in Table 3. These results show that peak intensities increased obviously in albizia under all conditions and in sugi after natural weathering without rainfall. Especially in albizia woods exposed to water, there was a considerable increase of carbonyl structures, indicating that residual lignin was drastically oxidized. Other peaks related to lignin (1240 and 830cm⁻¹ in albizia, C—O stretching and C—H out-of-plane deformation in the syringyl unit, respectively; 1270 and 810cm⁻¹ in sugi, C—O stretching and C—H out-of-plane deformation in the guaiacyl unit, respectively) also indicated the structural change of lignin.

The peak at around 1739cm⁻¹ was assigned to the carbonyl stretching vibration of carboxyl and ester groups, especially acetyl group binding to hemicellulose, such as xylan in hardwood and glucomannan in softwood.¹⁴ This peak remained after weathering, but its intensity decreased with the presence of water (Table 3); the wave-number of this peak shifted to 2–3cm⁻¹, presumably because of the reduction of acetyl group contents.

The relative intensities of the ESR signal are summarized in Table 4. A significant difference was observed between the two species based on the lignin results. In albizia wood, the intensities based on lignin increased after all exposure conditions. As the ESR signal of lignin was considered to be enhanced by the introduction of conjugated structures such as α -carbonyl group and quinoid,¹⁷ the formation of conjugated structures of lignin was believed to occur drastically in these samples, as observed by the IR analysis described above.

In sugi wood, however, the ESR intensity of the sample exposed to natural weathering without rainfall was considerably higher than in the samples exposed to natural weath-

Table 4. Relative intensities of ESR absorbances of surface fraction of weathered wood

Condition ^a	Relative intensity	Relative intensity per lignin
Albizia		
Unexposed	100.0	100.0
Natural	70.9	124.7
Natural without rainfall	164.9	195.4
Artificial	59.0	179.3
Sugi		
Unexposed	100.0	100.0
Natural	37.1	47.9
Natural without rainfall	112.0	132.0
Artificial	42.4	51.0

^aSee footnote of Table 1

ering with rainfall and artificial weathering, irrespective of a similar degree of lignin content and carbonyl generation. This result demonstrates that the structural change in the lignin polymer was different depending on the conditions (the presence or absence of water). Modification and breakdown of the lignin macromolecular network, such as side-chain cleavage, the aromatic ring opening, or both, would proceed in the presence of water; and as a result the reduction of radical stabilization occurred. Although a small amount of water was reported to enhance the formation of free radicals in wood,¹⁸ in our results for softwood sugi the oxidative change was observed only in the sample exposed to natural conditions without rainfall, and a marked change could be introduced by the presence of excess water. As water could not always be flashed at the same time as UV

irradiation during exposure, hydrolysis of susceptive bonding in lignin might occur by flashing water after lignin was activated by UV under the air-dried condition. Based on the results of this study, decomposition of lignin in sugi is accelerated by water itself, resulting in the fragmentation of lignin macromolecules.

Generally, deterioration of wood exposed to weathering has been believed to be mainly due to the decomposition of lignin in cell walls. Water such as rainfall was thought to play an important role, causing the formation of checks, cracks, and new surfaces, which are then exposed to UV irradiation during shrinking and swelling. Consequently, the decomposed lignin components would be easily leached out from the cell walls accompanied by erosion and discoloration. On the basis of our results, however, water flashing was proposed to accelerate the modification and decomposition of lignin polymer with UV irradiation, resulting in destruction of the lignin-hemicellulose matrix in cell walls. To improve the weathering properties of wood, protection against water and a shield against UV irradiation are needed.

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